

## **IMPROVED SILVER PLATING METHOD AND ARTICLES MADE THEREFROM**

[0001] This application claims priority under 35 U.S.C. §119(e) from following Provisional Applications, which are herein incorporated by reference: 60/412,301; 60/412,302; 60/412,303; and 60/412,306 all filed on September 20, 2002.

### **FIELD OF THE INVENTION**

[0002] The present invention relates to an improved, electroless silver plating method particularly suitable for the production of articles having antimicrobial and anti-static properties.

### **BACKGROUND OF THE INVENTION**

[0003] Metallization of organic substrates (e.g., polymeric materials) with silver and other noble metals is well known in the art. One such technique is described in U.S. Patent No. 3,877,965 to Broadbent et al., which describes metallizing nylon substrates with silver and is incorporated herein by reference. Articles metallized with silver have found a wide variety of uses due to the inherent antimicrobial and anti-static properties of silver. For example, silver plated nylon fibers are commonly woven into textile materials which in turn are used for consumer products (e.g., socks, wound dressings) and for electromagnetic interference (EMI) shielding applications for electronic equipment (e.g., cellular telephones, computers).

[0004] However, current processes for metallizing substrates with silver do have certain disadvantages. For example, the process described in Patent No: 3,877,965 has been found to exhibit several disadvantages. First, with most metallization processes, the pre-metallization steps require the tin salt (e.g., stannous or stannic chloride) to be dissolved with the aid of a

water-soluble alcohol (e.g., a C<sub>1</sub>-C<sub>4</sub> alcohol). The use of an alcohol results in significant evaporation problems.

[0005] A more significant problem is the use of a surfactant (e.g., sodium lauryl sulfate) during the metallization process. For example, the surfactant can lead to gelling of the plating bath if the bath temperature is too low. Likewise, the surfactant can cause significant foaming in the plating bath, which is difficult to remove after metallization is completed. Typically, foam generated during the metallization process ends up on the surface of the fibers. Once on the fiber surface, the foam becomes difficult to rinse off properly. This in turn potentially results in inhibiting silver ion release and also present adhesion issues due to the surface cracking when exposed to high temperatures. Cracking occurs as the contaminants (e.g., entrained air) are forced out under pressure from beneath the surface of the silver layer.

[0006] In addition, the use of a surfactant results in the color of the deposited silver being a very dark gray/silver (and sometimes even brown). This alternative color of the deposited silver lowers the aesthetic value of the product since consumers normally expect metallized silver to exhibit a bright metallic color.

[0007] However, one of the most significant problems associated with the use of a surfactant is the environmental impact and the associated costs of removing the surfactant from the waste effluent. Local sewer authorities, the Environmental Protection Agency (EPA) and other similar organizations now mandate very low discharge levels of "Methylene Blue Activated Substance" (i.e., MBAS). Surfactants such as sodium lauryl sulfate fall within the category of MBAS. In order to reduce MBAS to acceptable limits (typically 5 parts per million (ppm) or lower), significant effort and expense are required on waste treatment which in turn increase productions costs and time. Typically, removal of MBAS requires the use activated

charcoal chemistries along with high-grade adsorbent (activated charcoal) filters, which must be changed frequently due to clogging by particulate. Likewise, the amount of silver recovered from the waste is problematic because the recovered silver is in a low concentration as a percentage of the amount of sludge (e.g., around about 1 percent by weight).

[0008] In view of the disadvantages associated with surfactants, other metallization processes have been developed that use non-surfactant baths. Typically, these processes employ disodium ethylenediaminetetraacetic acid (EDTA) as a ligand instead of a surfactant. Representative patents relating to the use of disodium EDTA in silver plating are U.S. Patent Nos. 5,318,621 and 5,322,553, both assigned Applied Electroless Concepts. Another example is U.S. Patent No. 5,158,604 assigned to Monsanto Company. However, this technology is not without problems since high amounts of caustic soda must be used to dissolve and adjust pH of the plating bath.

### SUMMARY OF THE INVENTION

[0009] The present invention advantageously provides an improved method for plating an organic substrate with silver that avoids many of the disadvantages associated with prior silver plating methods. The method of the invention entails at least three (3) steps followed in sequence: (a) scouring; (b) pre-metallization; and (c) plating. Organic substrates to be plated can be in the form of fibers, a textile woven from fibers, or a polymeric foam (e.g., an open cell foam). In accordance with invention, the organic substrate is first scoured to prepare the surface for pre-metallization. Preferably, an aqueous cleaning solution is used.

[00010] Once the organic substrate has been sufficiently cleaned, the scoured, organic substrate is contacted with an aqueous, pre-metallization solution including a tin salt and an inorganic acid. In one embodiment, pre-metallization solution omits a water-soluble or water-

miscible solvent. In another embodiment, the pre-metallization solution omits a surfactant. Tin salts to be used include stannous chloride, stannic chloride, and mixtures thereof. Inorganic acids to be used include hydrochloric acid, sulfuric acid, and mixtures thereof.

[00011] The pre-metallized, organic substrate is thereafter plated with silver, which comprises: (i) contacting the pre-metallized, organic substrate with an aqueous  $\text{Na}_4\text{EDTA}$  solution; (ii) subsequently contacting the pre-metallized, organic substrate with an additional aqueous, silver salt solution to effect deposition of a silver oxide on the organic substrate, wherein the silver salt solution further includes a complexing agent; and (iii) contacting the organic substrate having the deposited silver oxide with a reducing agent thereby effecting formation of metallic silver on the organic substrate. Particularly preferred silver salts and complexing agents are silver nitrate and aqueous ammonia, respectively. A preferred class of reducing agents is reducing agents including an aldehyde functional group. Representative examples of reducing agents include formaldehyde, rochelle salts (sodium potassium tartrate), hydrazine, dextrose, triethanol amine, glyoxal, inverted sugar, glucose, sodium borohydride, dimethyl amineborane, hydrazine borane and mixtures thereof. In another embodiment, all of the solutions in the plating step preferably omit a surfactant

[00012] The present invention also provides articles prepared in accordance with the method of the invention. In one embodiment, the organic substrate further includes at least one layer of a non-noble metal disposed thereon, and is preferably disposed on the plated metallic silver layer. One particularly preferred non-noble metal is copper. In accordance with the invention, the metallic silver layer is least 5 percent by weight of the article, with at least 10 percent by weight being more preferred.

[00013] Advantageously, the method of the invention allows the use of surfactants to be omitted while increasing the recovery of silver from waste products. Thus, environmental concerns can be alleviated through the use of the invention as compared to prior processes.

#### BRIEF DESCRIPTION OF THE DRAWING

[00014] FIG. 1 is an electron micrograph at 960x magnification of nylon fibers plated with the silver using the method of the invention.

[00015] FIG. 2 is an electron micrograph at 5000x magnification of nylon fibers plated with the silver using a prior art process.

#### DETAILED DESCRIPTION OF THE INVENTION

[00016] The present invention provides an improved method for plating an organic substrate with metallic silver while avoiding many of the disadvantages associated with the prior art. The method of the invention entails first scouring the organic substrate to prepare the surface for pre-metallization. Once the organic substrate has been sufficiently scoured, the organic substrate is contacted with an aqueous, pre-metallization solution including a tin salt and an inorganic acid. Plating is thereafter accomplished by contacting the pre-metallized, organic substrate with an aqueous  $\text{Na}_4\text{EDTA}$  solution that in turn is followed by contacting the pre-metallized, organic substrate with an aqueous, silver salt solution to effect deposition of a silver oxide on the organic substrate. The silver salt solution further includes a known complexing agent. The deposited silver oxide is converted (i.e., reduced ) to metallic silver by contacting the organic substrate with a reducing agent thereby effecting formation of metallic silver.

**[00017]** In accordance with the invention, organic substrates to be metallized with silver include any organic material capable of receiving a deposited metallic layer. The organic material can be synthetic or natural with synthetic (e.g., polymeric) materials being preferred. Examples of synthetic polymeric materials to be used include, but are not limited to, nylon, polyester, acrylic, rayon, and polyurethane. Examples of natural materials include, but are not limited to, cellulose, and silk. The organic materials can be in any physical form capable of receiving the deposited metallic layer. For example, the organic material can be in the form of filaments, fabrics, staple, chopped fibers, micronized fiber, foams, particulates and filler materials. Preferably, the organic material is in the form of a fiber or filament, or a textile matrix made therefrom. If the organic material is in the form of a foam, an open-cell foam (i.e., has a three-dimensional interconnected network of cells) is preferred to allow metallization throughout.

**[00018]** The organic substrate is first prepared for pre-metallization by scouring to remove debris and/or to remove any coatings or film on the material that may interfere with metallization. Scouring is a technique well known in the art and thus does not require much discussion. Typically, the material is washed with an aqueous cleaning solution that may or may not contain a surfactant (e.g., a nonionic surfactant). In accordance with the invention, reference to "aqueous" means at least a majority of the medium is water with the remaining portion being a water-soluble or water-miscible organic solvent. The organic material can also be abraded using a scouring brush or equivalent device. In a preferred embodiment, scouring is accomplished with a high-speed water spray, which facilitates in-line processing and avoids the necessity of a scouring brush.

[00019] Once the organic substrate has been sufficiently scoured, the material is subjected to pre-metallization with an aqueous solution of a tin salt and an inorganic acid. As will be apparent to one skilled in the art, such a solution is often referred to as a “sensitizing” solution. However, unlike prior art “sensitizing” solutions, the pre-metallization solution preferably omits a surfactant and/or a water-soluble or water-miscible organic solvent such as a C<sub>1</sub>-C<sub>4</sub> alcohol. Preferably, the tin salt is a halide such as stannous chloride, stannic chloride, or mixtures thereof. Examples of inorganic acids include, but are not limited to, hydrochloric acid, sulfuric acid, and mixtures thereof. In a more preferred embodiment, the tin salt is stannous chloride and the inorganic acid is hydrochloric acid. Ranges of the two components are set forth in Table 1:

Table 1		
	Tin Salt (grams/liter)	Inorganic Acid (% by Volume)
Preferred	1-30	1-20
More Preferred	2-25	3-18
Optimal	4-20	6-15

[00020] Once the organic substrate has been pre-metallized, the organic substrate is preferably washed to remove excess salt and acid from the organic substrate that can interfere with subsequent metallization. For example, the organic substrate can be washed with a counter flow rinse with controlled water flow. This enables the removal of any excess salts and acids from the substrate material while leaving optimal amount of activated sites on the surface of the substrate. Preferred levels of water flow to wash the substrate range from about 25 to about 55 gallons per minute (gpm), with 30 to 50 gpm being more preferred, and 35 to 45 gpm being more preferred.

[00021] In accordance with the present invention, metallization is accomplished in three (3) substeps. An aqueous tetrasodium ethylenediaminetetraacetic acid ( $\text{Na}_4\text{EDTA}$ ) is prepared into which the pre-metallized organic substrate is contacted preferably by immersing the substrate in the aqueous solution. The aqueous solution is preferably prepared using de-ionized (DI) water to avoid possible contamination. The DI water should have a resistance of about 0.4 to about 20 megaohms, with 0.8 to 10 megaohms being preferred, and 3 to 7 megaohms being more preferred. The concentration of the aqueous  $\text{Na}_4\text{EDTA}$  solution should range from about 5 to about 30 percent by weight (wt. %), with 10 to 25 wt. % being preferred, and 10 to 20 wt. % being even more preferred. Preferably, the  $\text{Na}_4\text{EDTA}$  solution omits a surfactant as is typically found in conventional silver plating processes. Likewise, the  $\text{Na}_4\text{EDTA}$  solution also preferably omits caustic soda as typically found in  $\text{Na}_2\text{EDTA}$  solutions. Advantageously, the use of  $\text{Na}_4\text{EDTA}$  facilitates the deposition of metallic silver with a tighter grain structure, which in turn leads to a relatively smoother surface as evidenced by examination of silver-plated nylon fiber by electron microscopy. Likewise,  $\text{Na}_4\text{EDTA}$  allows a surfactant to be omitted thus alleviating environmental concerns regarding levels of surfactant in the waste effluent.

[00022] An aqueous silver salt solution is also prepared for subsequent contacting of the organic substrate. Preferably, the organic substrate is contacted with the silver salt solution by adding the silver salt solution directly to the bath containing the organic substrate and the aqueous  $\text{Na}_4\text{EDTA}$  solution. Thus, the organic substrate is contemporaneously immersed in both solutions, which is referred to as the "metallization bath." Alternatively, the organic substrate can be removed from the  $\text{Na}_4\text{EDTA}$  solution and subsequently immersed in the silver salt solution. One particularly preferred silver salt is silver nitrate (i.e.,  $\text{AgNO}_3$ ). The silver salt solution additionally includes a complexing agent as known in the art, which form a complex *in*



*situ* with the dissolved silver salt. One particularly preferred complexing agent is aqueous or aqua ammonia (i.e.,  $\text{NH}_4\text{OH}$ ) which is commonly used as a complexing agent for silver nitrate. As with the  $\text{Na}_4\text{EDTA}$  solution, the silver salt solution preferably omits a surfactant.

[00023] The silver salt solution is preferably prepared by first dissolving the silver salt in water. Once the silver salt has been dissolved, the complexing agent is added to the solution. A precipitate of a silver oxide can form and is re-dissolved through the addition of excess complexing agent. The addition of excess complexing agent is believed to form a complex of the silver salt and the complexing agent. For example, when silver nitrate and aqua ammonia are used, a precipitate of silver oxide forms *in situ* which is re-dissolved upon the addition of excess aqua ammonia to provide a metallization bath having a light amber color. Preferred initial weight/volume ratios of silver salt (i.e.,  $\text{AgX}$ ) to water ( $\text{H}_2\text{O}$ ) and of percent by volume of complexing agent are set forth in Table 2. Preferred molar ratios of silver salt to complexing agent in the final metallization bath (i.e., upon re-dissolution of the silver precipitate) are set forth in Table 3.

Table 2		
	AgX:H <sub>2</sub> O (weight:volume)	Complexing Agent (percent by volume)
Preferred	0.25:2 to 1.75:2	17 to 38
More Preferred	0.5:2 to 1.5:2	20 to 35
Optimal	0.75:2 to 1.25:2	25 to 31

Table 3	
	Molar Ratio of Complexing Agent:AgX
Preferred	2.5:1 to 5.5:1
More Preferred	3:1 to 5:1
Optimal	3.5:1 to 4.5:1

[00024] In accordance with the invention, immersion of the organic substrate in the metallization bath results in the deposition of silver oxide on the substrate surface. As will be apparent to one skilled in the art, deposition can be confirmed by a visual inspection of the substrate undergoing a change in color due to the deposited silver oxide. For example, in the case of  $\text{AgNO}_3:\text{NH}_3$  one will typically observe the substrate to develop a shade of brown on the surface which correlating to a silver oxide layer. Preferably, the organic substrate is immersed in the metallization bath prior to the addition of the reducing agent for about 30 seconds, with 20 seconds being more preferred. The temperature of the metallization bath is not critical and can range from about 15 to about 45°C, with 20 to 30°C being more preferred. These parameters can be easily determined by one skilled in the art.

[00025] The organic substrate with the silver oxide thereon is subsequently contacted with a reducing agent to convert the silver oxide to metallic silver. Preferably, contacting is accomplished by adding the reducing agent directly to the metallization bath. Alternatively, the organic substrate is removed from the metallization bath and is separately contacted (e.g., immersed) with an aqueous solution of the reducing agent. Reducing agents to be used in accordance with the invention are well known in the art. Examples of reducing agents to be used include, but are not limited to, formaldehyde, rochelle salts (sodium potassium tartrate), hydrazine, dextrose, triethanol amine, glyoxal, inverted sugar, glucose, sodium borohydride, dimethyl amineborane, hydrazine borane. More preferred are reducing agents containing an aldehyde functional group such as formaldehyde. In the case where  $\text{AgNO}_3:\text{NH}_3$  is used, the addition of the reducing agent (e.g., formaldehyde) results in the silver oxide layer on the substrate changing color to a bright gold or gray-gold color as the silver oxide is converted to metallic silver. Preferably, the amount of reducing agent to be used ranges from about 5 to about

40 percent by weight of substrate, with 6 to 25 percent by weight being preferred, and 8 to 22 percent by weight being more preferred.

[00026] Once sufficient metallic silver has been converted, the organic substrate is removed from the metallization bath and washed. Preferably, the silver-plated substrate is immersed in hot water. The silver-plated substrate is then preferably immersed in a weak solution of sodium hydroxide, which brightens the silver plating to a light gold color or a light gray color. This indicates that a pure layer of silver deposited on the substrate. The article can be subjected to multiple rinse cycles to ensure the cleanliness of product.

[00027] As will be apparent to one skilled in the art, the amount of metallic silver deposited on the organic substrate is a function of immersion time. In accordance with the invention, the time for complete deposition of the metallic silver layer will be less than 4 hours. However, time periods for immersing the substrate in the various solutions can easily be altered depending on the amount of deposited silver desired. The amount of silver deposited on the organic substrate can range from 0.1% to 15% by weight, depending on the specific characteristics desired for the final product. Preferably, the deposited silver layer is at least 5 percent by weight, with at least 10 percent by weight being more preferred. The actual amount of silver deposited on the substrate is easily calculated by a simple titration such as the Vollar process.

[00028] Unlike the prior art process of U.S. Patent No: 3,877,965, the remaining metallization bath is treated with ease. The pH of the metallization bath is raised to approximately 13 which results in the dissolved silver being converted into a colloidal form. The pH is then lowered to around 2 typically with the help of an inorganic acid (e.g., sulfuric acid).

The colloidal silver precipitates and settles down at the bottom of the container after several hours. The purity of the silver precipitated has been found to be up to 50 percent by weight.

[00029] As will be apparent to one skilled in the art, the adhesion of the plated silver is easily ascertained. One simple test for adhesion of the silver to the substrate requires placing a sample into an oven at 200°C for about 5 minutes and then boiling the same sample for 1 hour in water. The resistance of the sample before and after heating and boiling are compared. A variation in resistance of no more than about 20 percent indicates excellent adhesion. In a more preferred embodiment, the variation of resistance is no more than 10 percent.

[00030] In another embodiment of the invention, the silver-plated substrate is additionally plated with a non-noble metal such as copper as described in U.S. Patent No. 3,877,965. Copper is auto-catalytic on silver and thus can reduce itself easily for form a copper layer. Using such process up to 30% by weight of copper is deposited on to the silver-plated substrate. Commercial plating solutions are available from Atotech USA, Enthone OMI, and MacDermid Corporation.

[00031] The following non-limiting examples illustrate the use of the method of the invention to plate organic substrates with metallic silver layers.

### EXAMPLES

#### Example 1

[00032] A 30/10 knit sample of nylon weighing 25 grams was scoured to remove any contaminants. The knit sample was wrapped into a skein and scoured in counter flow de-ionized

water. The sample was pre-metallized with a solution containing 1 % by volume HCL and 10 grams of anhydrous tin chloride ( $\text{SnCl}_2$ ) for about 2 minutes. A silver salt solution was prepared by dissolving 0.04 grams of silver nitrate (0.1 % silver by weight target) in de-ionized water. The silver salt was then complexed with 0.045 mL of 27 % by volume aqua ammonia. A tetrasodium EDTA solution was prepared by dissolving 0.002 grams  $\text{Na}_4\text{EDTA}$  in 1 liter of de-ionized water. The skein was placed in the reactor containing the  $\text{Na}_4\text{EDTA}$  solution and made to revolve. The silver salt solution (i.e., complexed silver nitrate and ammonia) was added to the reactor slowly until all contents were emptied. This was followed by 0.016 mL formaldehyde. After three hours the sample was removed and subjected to hot water rinse. A 0.1 % by volume NaOH solution (1 liter) was prepared with a temperature of 70°C. The metallized skein was then dipped into the solution and rinsed thoroughly. The sample was subjected to Dow Corning Corporate Test Method 0923: organism - *Staphylococcus aureus* ATCC 7538; sample size - 0.75 grams; results - percent reduction in colony >99.9%.

## Example 2

[00033] As in example 1, a 30/10 knit sample of nylon weighing 25 grams was scoured to remove any contaminants. The knit sample was wrapped into a skein and scoured in counter flow de-ionized water. The sample was pre-metallized with a solution containing 1 % by volume HCL and 10 grams of anhydrous tin chloride ( $\text{SnCl}_2$ ) for about 2 minutes. A silver salt solution was prepared by dissolving 1.95 grams of silver nitrate (5 % silver by weight target) in de-ionized water. The silver salt was then complexed with 2.25 ml of 27 % by volume aqua ammonia. A tetrasodium EDTA solution was prepared by dissolving 0.1 grams of  $\text{Na}_4\text{EDTA}$  in 1 liter of de-ionized water. Skein was placed in the reactor containing the  $\text{Na}_4\text{EDTA}$  solution

and made to revolve. The silver salt solution (i.e., complexed silver nitrate and ammonia) was added to the reactor followed by 0.8 mL of formaldehyde. After three hours the sample was removed and subjected to hot water rinse. The metallized skein was rinsed in a NaOH solution as in Example 1. The sample was subjected to Dow Corning Corporate Test Method 0923: organism - *Staphylococcus aureus* ATCC 7538; sample size - 0.75 grams; results - percent reduction in colony >99.9%.

### Example 3

**[00034]** A 25 grams sample of ripstop fabric was processed following the procedure of examples 1 and 2. The silver-plated sample was then subjected to Dow Corning Corporate Test Method 0923: organism - *Staphylococcus aureus* ATCC 7538; sample size - 0.75 grams; results - percent reduction in colony >99.9%.

### Example 4

**[00035]** A 25 gram sample of filler material including nano powders (i.e., powder made from nylon and polyethylene) was processed following the procedure of examples 1 and 2. The silver-plated sample was then subjected to Dow Corning Corporate Test Method 0923: organism - *Staphylococcus aureus* ATCC 7538; sample size - 0.75 grams; results - percent reduction in colony >99.9%.

## Example 5

[00036] A 30/10 knit sample of nylon weighing 118 grams was scoured to remove any contaminants. The knit sample was wrapped into a skein and scoured in counter flow de-ionized water. The sample was pre-metallized with a solution containing 10 % by volume HCL and 100 grams of anhydrous tin chloride ( $\text{SnCl}_2$ ) for about 2 minutes. A silver salt solution was prepared by dissolving 45 grams of silver nitrate (about 22 % silver by weight target) in de-ionized water. The silver salt was then complexed with 52 mL of 27 % by volume aqua ammonia. A tetrasodium EDTA solution was prepared by dissolving 2.2 grams  $\text{Na}_4\text{EDTA}$  in 6 liters of de-ionized water. The skein was placed in the reactor containing the  $\text{Na}_4\text{EDTA}$  solution and made to revolve. The silver salt solution (i.e., complexed silver nitrate and ammonia) was added to the reactor slowly until all contents were emptied. This was followed by 18 mL of formaldehyde. After three hours the sample was removed and subjected to hot water rinse. A 0.1 % by volume NaOH solution (5 liters) was prepared with a temperature of 70°C. The metallized skein was then dipped into the solution and rinsed thoroughly. The color changed to light almost gold colored silver. The sample was dried and then sent for an adhesion check. The results were as follows: as is - 484 Ohms (50 cm distance) using a Keithley 580 micro-ohmmeter; after heat - 345 Ohms; and after boil - 365 Ohms.

## Example 6

[00037] A sample obtained from the silver-plated materials from example 5 was cut to make a 1.5 gram sleeve. The sleeve was then placed in a beaker with 5 % by volume sodium

chloride solution for a 24-hour period. The solution after the 24-hour period was then tested for silver ions using a Perkin Elmer Analyst 300. The same test was repeated over a period of 7 days. The release of ions was consistent each day at 0.5 ppm illustrating the sustained release of silver prepared in accordance with the invention.

#### Example 7

[00038] A sample obtained from the silver-plated materials from example 5 was cut to weigh 0.75 grams and subjected to Dow Corning Corporate Test Method 0923. Organism used was *Staphylococcus aureus* ATCC 6538. The sample reduced organism growth by over 99.9%.

#### Example 8

[00039] A 210/34 knit nylon sample weighing 118 grams was cleaned. The sample was wrapped into a skein and scoured with a counter flow of de-ionized water. The skein was pre-metallized in a solution of 10 % by volume HCL and 100 grams of anhydrous tin chloride ( $\text{SnCl}_2$ ) for 2 minutes. A silver salt solution was prepared by dissolving 45 grams of silver nitrate in de-ionized water. The silver salt was then complexed with 52 ml of 27 % by volume aqua ammonia. A tetrasodium EDTA solution was prepared by dissolving 2.2 grams of  $\text{Na}_4\text{EDTA}$  in 6 liters of de-ionized water. Skein was placed in the reactor containing the  $\text{Na}_4\text{EDTA}$  solution and made to revolve. The silver salt complex was added to the reactor and followed by 18 mL of formaldehyde. After three hours the sample was removed and subjected to hot water rinse. As in the previous examples, a 0.1% by volume NaOH solution was prepared and the metallized skein was dipped into the solution. The color changed from grey to a light almost gold colored silver.



[00040] The silver-plated sample was then metallized with commercially available copper chemistry from Atotech USA. The metallization process was carried out following the instructions suggested by supplier. Completion of the deposition of copper can be visually determined when the bath changes color from a deep blue to colorless, which indicates a complete reduction of the metal.

[00041] A 10.6 grams sample of the silver-copper material was then cut and placed in a beaker filled with 2.1 grams of Rochelle salt (i.e., sodium potassium tartrate) dissolved with de-ionized water. A silver salt complex made up of 3.6 grams of silver nitrate and 4.3 mL of aqua ammonia was then poured into the sample under constant agitation. The pink color of silver-copper changed to a light brown at this time. A few drops of further diluted aqua ammonia were added drop wise into the bath with an ink dropper under constant agitation. The color of the sample then started to change to a dull white and eventually a bright white color. This step took about 35 minutes to complete. At that time sample is removed from bath and rinsed thoroughly with de-ionized water for 15 minutes. Silver was calculated to provide a 15% by weight gain. The resistance of the material after deposition of each metallic layer was also recorded; resistance with Silver - 80 Ohms/50 cm using a Keithley 580 micro-ohmmeter; resistance with Silver-Copper - 25 Ohms/50 cm; and resistance with Silver-Copper-Silver - 18 Ohms/50 cm.

#### Example 9

[00042] A sample of the silver-copper-silver material from example 8 was cut into a 1.5 gram sleeve. The sleeve was then placed in a beaker with 5 % by volume sodium chloride solution for a 24-hour period. The solution after a 24-hour period was then tested for silver and

copper ions using a Perkin Elmer Analyst 300. The same test was repeated over a period of 7 days. The release of ions was consistent each day at 2 ppm of silver and 3 ppm of copper.

#### Example 10

[00043] A sample of the silver-copper-silver material from example 8 was cut to weigh 0.75 grams and subjected to Dow Corning Corporate Test Method 0923. Organism used was *Staphylococcus aureus* ATCC 6538 and the material caused a reduction of organism growth by over 99.9%.

#### Example 11

[00044] A quenched foam sample weighing 11.8 grams was cleaned with non-ionic surfactant Triton X-100 and rinsed thoroughly. A 83 % by weight sulfuric acid solution was prepared and the foam was dipped in the solution for 25 seconds to 45 seconds to ensure proper etching of the surface. Immediately the sample was rinsed with copious amounts of de-ionized water. The foam was pre-metallized with solution containing 12 % by volume HCL and 120 grams of anhydrous tin chloride ( $\text{SnCl}_2$ ) for 2 minutes. The foam sample was then rinsed in counter flow de-ionized water. A tetrasodium EDTA solution was prepared by dissolving 0.22 grams of  $\text{Na}_4\text{EDTA}$  was dissolved in 2 liters of de-ionized water. The pre-metallized foam was placed in reactor containing the  $\text{Na}_4\text{EDTA}$  solution and made to revolve. A silver salt solution was prepared by dissolving 4.5 grams of silver nitrate in de-ionized water. The silver salt solution was then complexed with 5.2 mL of 27 % by volume aqua ammonia. The silver salt complex was added to the reactor and followed by 18 mL of formaldehyde. After three hours the sample was removed and subjected to hot water rinse. The metallized foam was dipped into a NaOH solution as prepared in the previous examples. The color changed to a dull, white silver.

Sample was dried and evaluated for resistance. The silver-plated foam exhibited a resistance of 0.5 Ohms/50 cm using a Keithley 580 micro-ohmmeter.

#### Example 12

[00045] Samples of silver-plated fiber prepared in accordance with the invention were compared to silver-plated fibers prepared following the procedure set forth in U.S. Patent No. 3,877,965. Samples of both samples of fiber were examined with a scanning electron microscope. A photomicrograph of the inventive fibers is found in FIG. 1, while a photomicrograph of the comparative fibers is found in FIG. 2. As can be clearly seen from the photomicrographs, the fibers plated with the inventive method exhibit a smoother surface as compared to fibers prepared with the prior art process. This is believed due to the tighter grain structure of the silver plating provided by the method of the present invention.